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FACULTY OF ENGINEERING AND ARCHITECTURE

# Positive effect of hydrogen co-feeding on the catalytic dehydrogenation of propane over Pt

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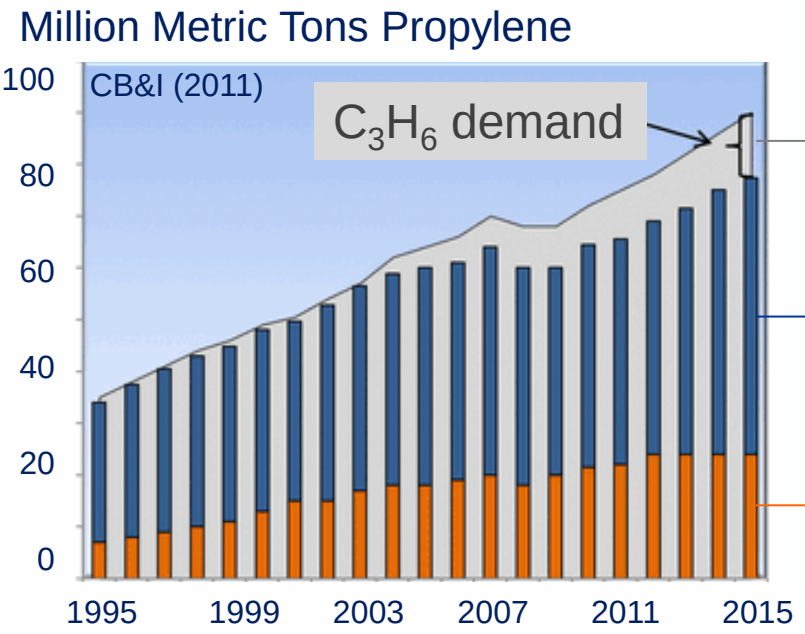
ICTAC-16, Zakopane, 21/06/2016

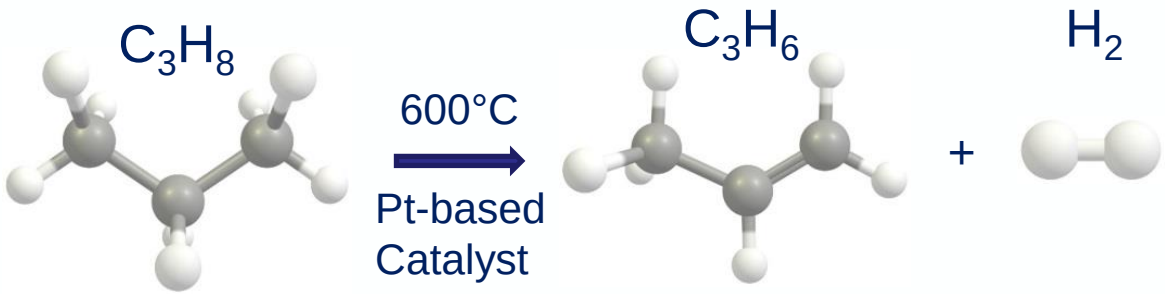
# Catalytic propane dehydrogenation




Production gap → Need of on-purpose production route such as catalytic dehydrogenation of propane

Production via steam cracking (low selectivity)

Production via Fluid Catalytic Cracking (low selectivity)




- ✓ Sufficient $C_3H_6$ selectivity (~80%)
- ✗ Low activity for dehydrogenation
- ✗ Fast catalyst deactivation

- ✓ Alloying with promoting element (e.g. Ga)
- ✓ Co-feeding of $H_2$

# Co-feeding $H_2$ (experiments)

$C_3H_8$ dehydrogenation experiments on Pt-based catalyst

Input conditions

| | | Siddiqi (2010) and Sun (2010) |
|---|---|---|
| Temperature | | 873 K |
| Total pressure | | 1.013 bar |
| Partial pressures | $C_3H_8$ | 0.20 bar |
| | $H_2$ | 0.25 bar |
| Catalyst weight | | 0.025 g |
| Molar flowrates | $C_3H_8$ | 0.029 mol/hr |
| | $H_2$ | 0.037 mol/hr |
| | He | 0.081 mol/hr |
| Active sites | | 0.03 $mol_{active\ sites}/kg_{cat}$ |
| Pt dispersion | | 84 % |
| Pt wt% in catalyst | | 0.7 wt% |

Possible explanations

(1) Reduced blocking of active sites

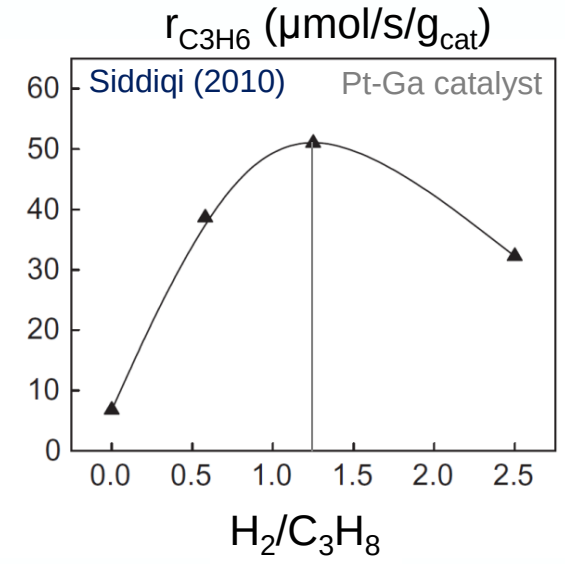
(2) Coverage dependence of energies

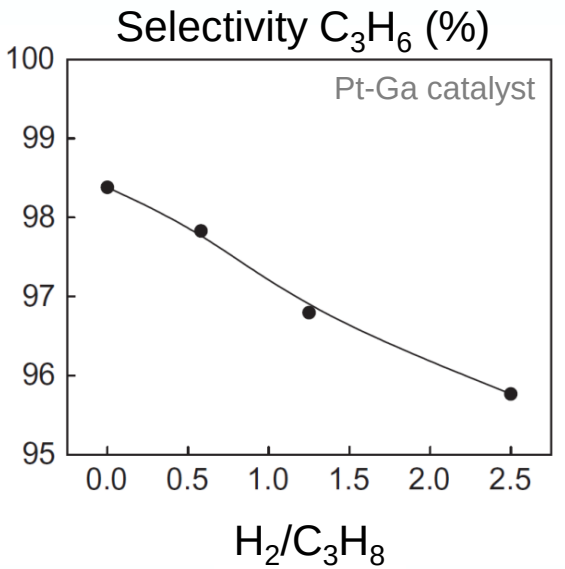
(3) Hydrogen assisted β-hydrogen abstraction

(4) Subsurface hydrogen

GOAL

Explain the 'positive hydrogen effect' using DFT kinetics for an extended reaction network



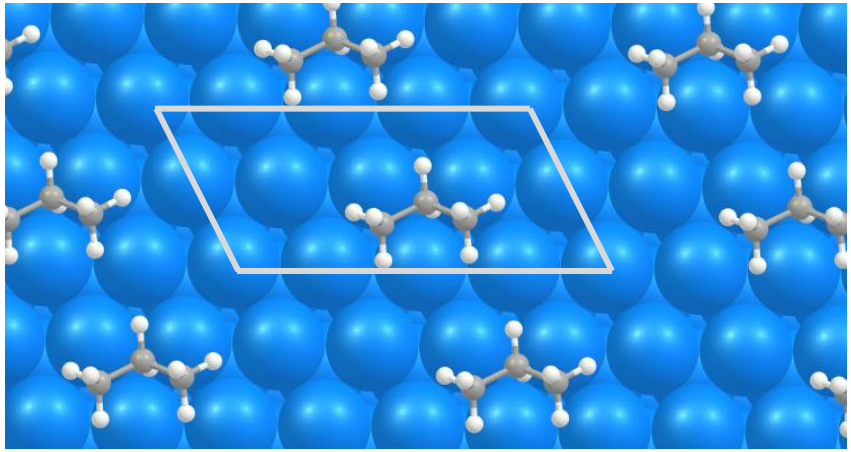

Siddiqi, G.; Sun, P. P.; Galvita, V.; Bell, A. T., *J. Catal.* 2010, 274, (2), 200-206.

# Computational approach

Density Functional Theory (DFT) calculations with periodic slab approach

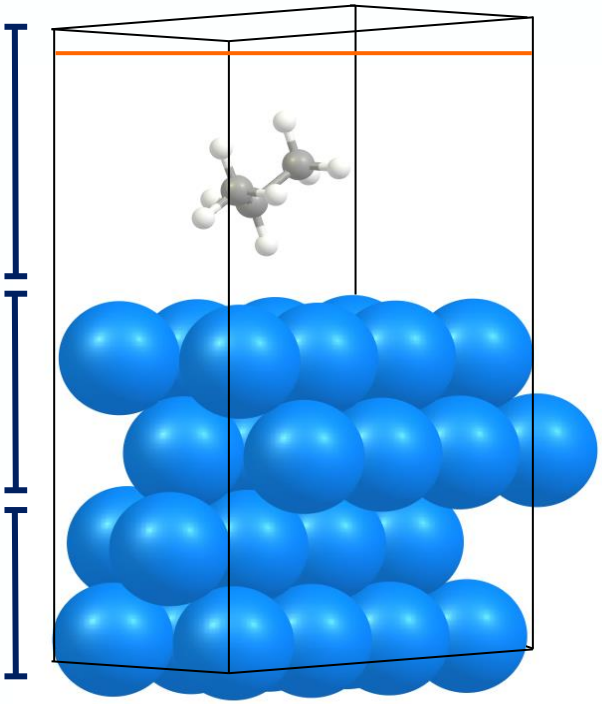
- optPBE vdW-DF functional (long range interactions) (Dion 2004 and Klimes 2010)
- 4×2 Pt(111) unit cell

top view



1 propylene/8 Pt atoms:
Half of experimental monolayer coverage
(Lee 2001, Tsai 1997)

side view




- Plane waves, PAW, 400 eV cut-off, no spin polarization
- First order Methfessel-Paxton smearing, σ=0.20 eV
- 3×5×1 k-point Monkhorst-Pack grid
- TS determination: NEB, followed by dimer calculation
- *S*, *H*: statistical thermodynamics based on harmonic oscillator approach

# Microkinetics and reactor modelling

## Rate coefficients

Transition state theory

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta^{\ddagger} S}{R}\right) \exp\left(-\frac{\Delta^{\ddagger} H}{RT}\right)$$

Reaction products calculated in separate unit cells

## Reactor model

CSTR reactor model:

$$F_{i_0} - F_i + V \cdot r_i = 0$$

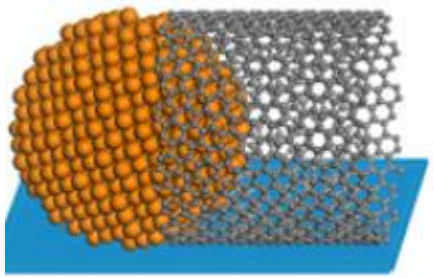
## Kinetic model

- Surface species: $\frac{d\theta_i^*}{dt} = R_{i^*} = 0$
- Pseudo-Stationary State Approximation (PSSA)
- All reaction steps are reversible
- 40 reactions in total

| Type of reaction | Example |
|---|---|
| Ad-/desorption | $C_3H_8 \rightleftharpoons C_3H_{8,physi}$ |
| Dehydrogenation | $C_3H_{8,physi} \rightleftharpoons CH_3\text{-}\underset{\vert}{\overset{\vert}{CH}}\text{-}CH_3 + H\text{-}\underset{\vert}{Pt}$ (Pt, Pt) |
| C-C scission | $CH_3\text{-}\underset{\vert}{CH}\text{-}CH_3 \rightleftharpoons CH_3\text{-}\underset{\vert}{Pt} + CH\text{-}\underset{\Vert}{Pt_2}\text{-}CH_3$ |
| Isomerization | $CH_3\text{-}\underset{\vert}{CH}\text{-}CH_3 \rightleftharpoons CH_2\text{-}\underset{\vert}{CH_2}\text{-}CH_3$ |
| Deep dehydrogenation | $CH_2\text{-}\underset{\vert}{CH}\text{-}CH_3 \rightleftharpoons CH_2\text{-}\underset{\Vert}{C}\text{-}CH_3 + H\text{-}\underset{\vert}{Pt}$ |
| Coke formation | $C \rightarrow$ coke formation, $\underset{\Vert\Vert\Vert}{Pt_3}$ |

## Coke formation reaction

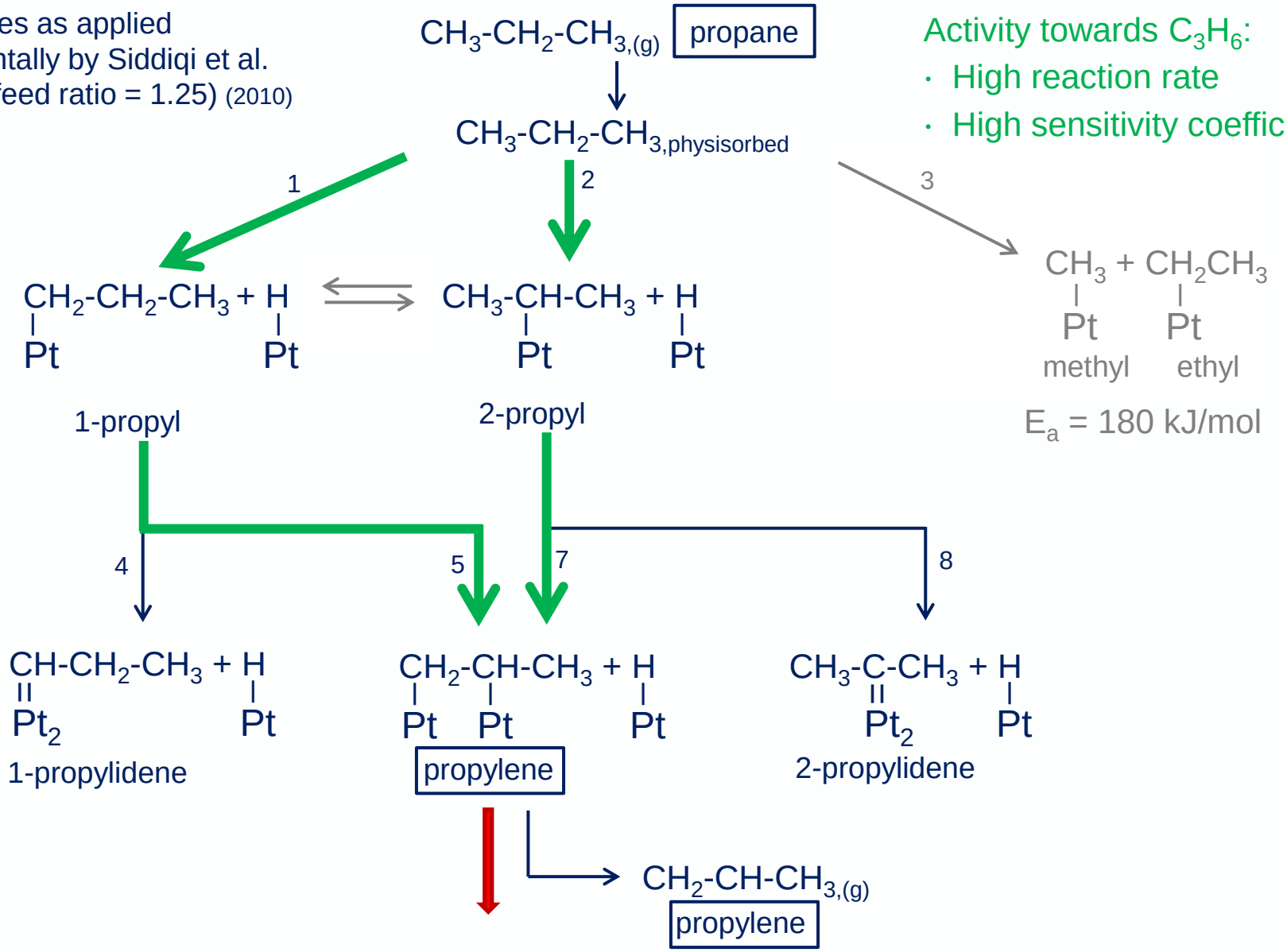
- Too complex to include in ab initio network
- Rate coefficient = experimental coke formation



Peng (2012)

# Reaction path analysis

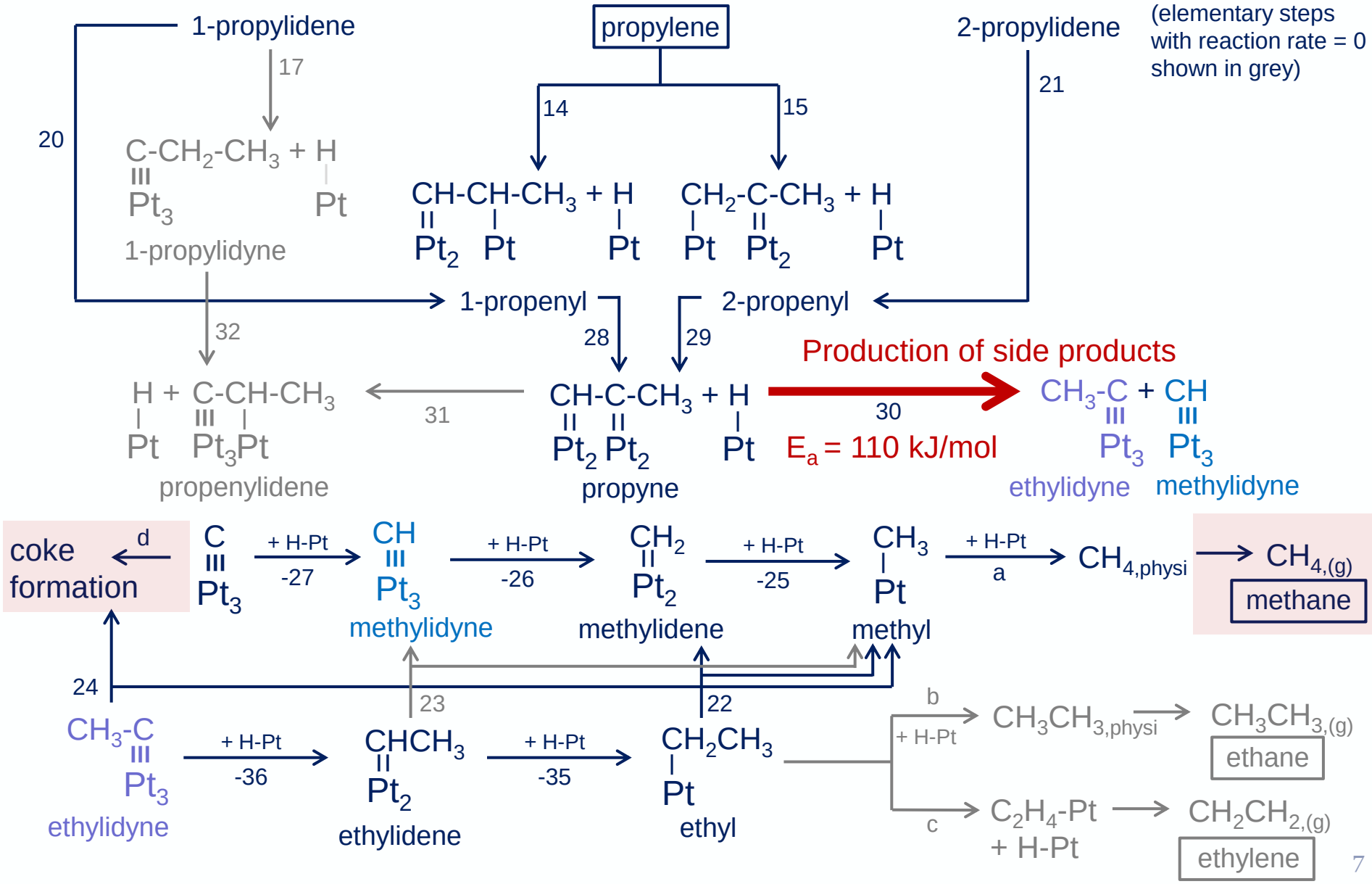
Input values as applied experimentally by Siddiqi et al. ($H_2/C_3H_8$ feed ratio = 1.25) (2010)




Activity towards $C_3H_6$:

- High reaction rate
- High sensitivity coefficient

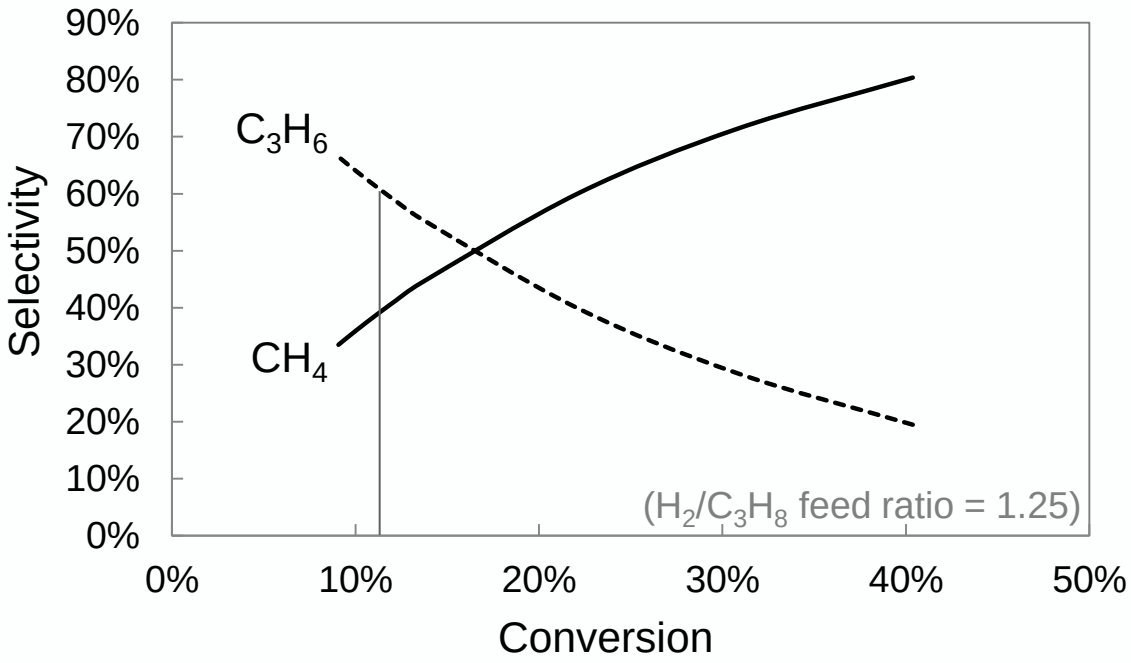
# Reaction path analysis



# Base case simulation

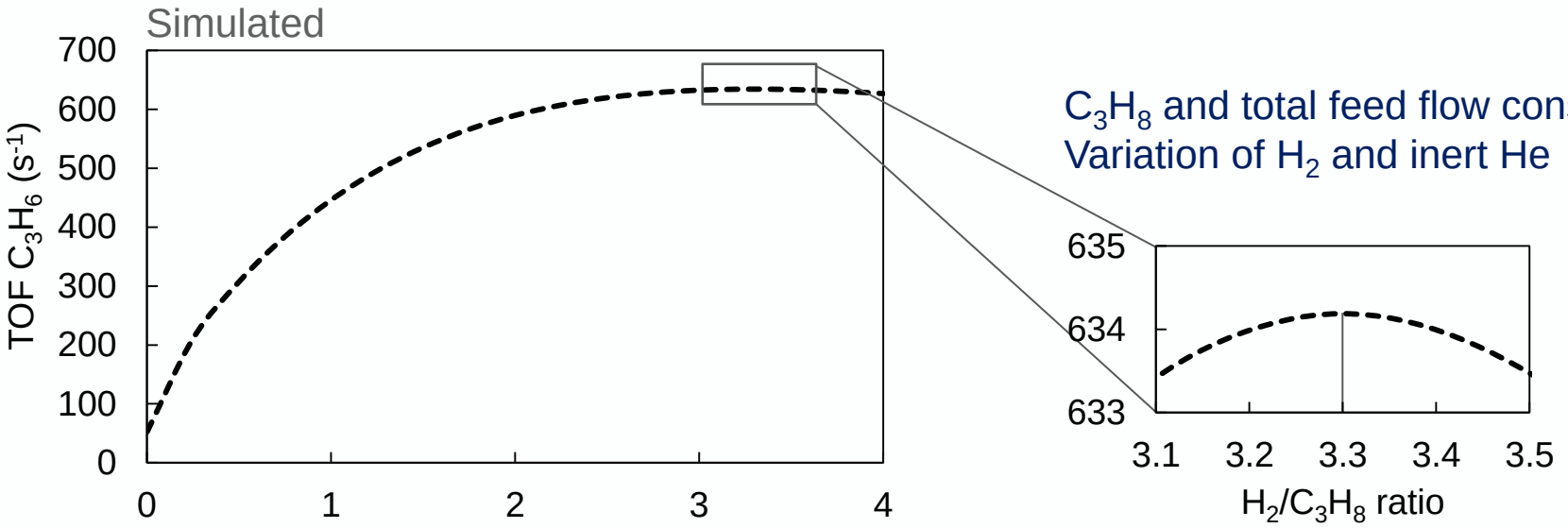
Experimental input by Siddiqi et al. ($H_2/C_3H_8$ = 1.25) (2010)

✓ Conversion-selectivity relation and coke formation

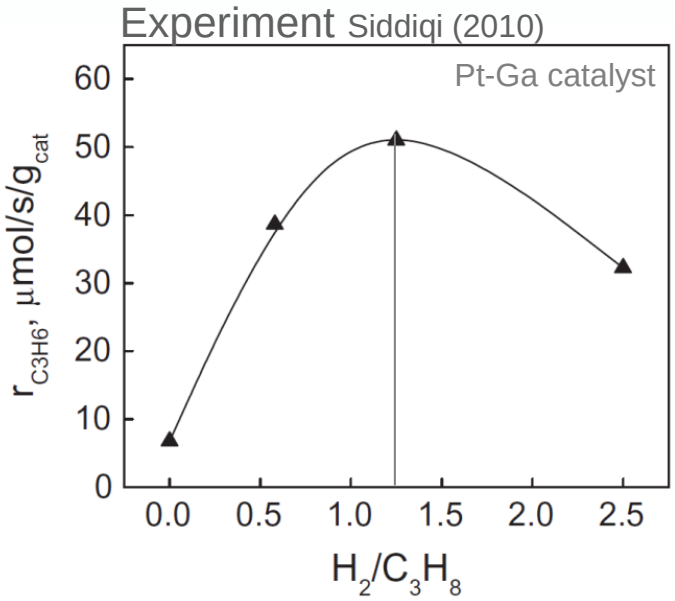



| | Experiment | Simulated |
|---|---|---|
| Conversion (%) | 11.5 | 11.7 |
| Selectivity $C_3H_6$ (%) | 79.0 | 60.0 |
| TOF ($s^{-1}$) | 1.0 | 496.0 |
| Coke formation (5' TOS) ($mol_C/mol_{Pt,surface}$) | 32.0 | 32.6 |

# Variation of $H_2$ pressure




$C_3H_8$ and total feed flow constant
Variation of $H_2$ and inert He

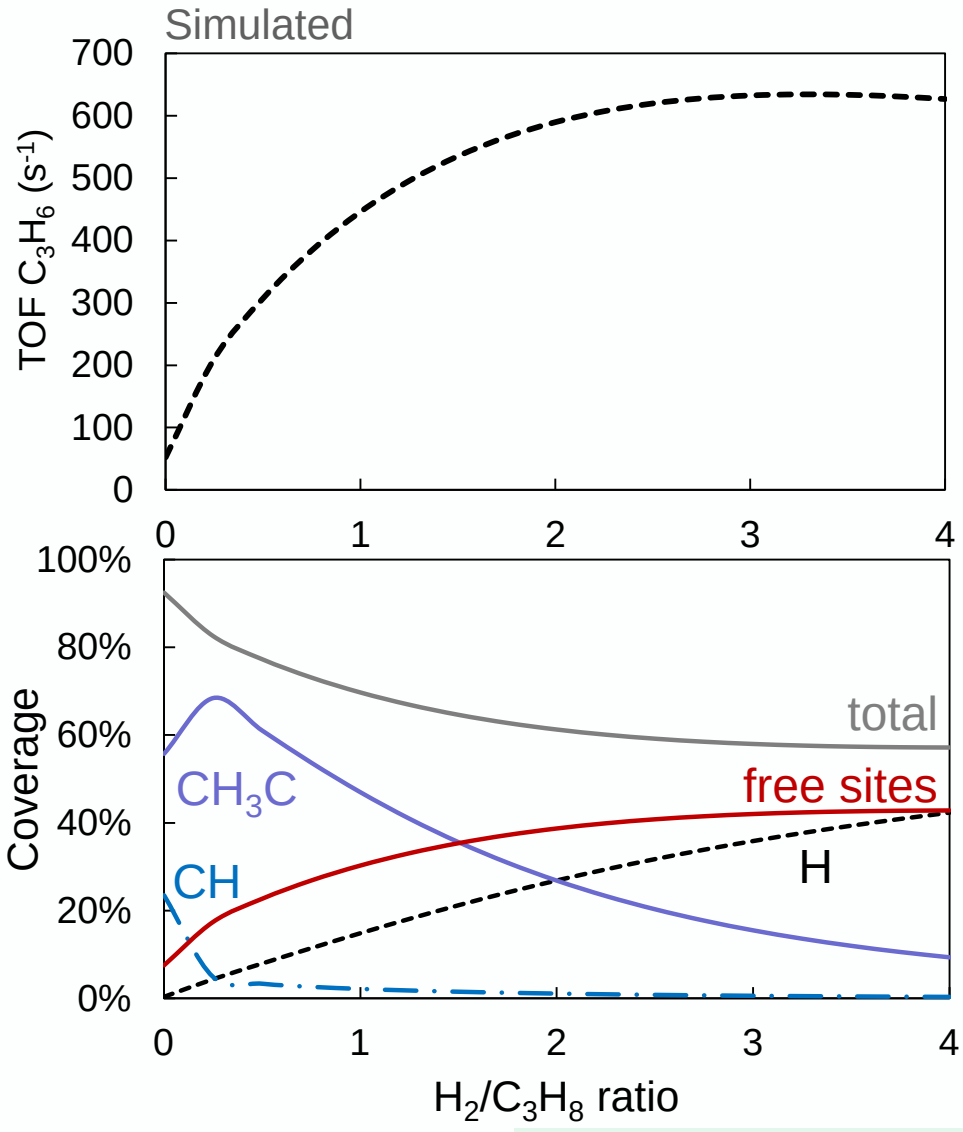



- Increasing TOF of $C_3H_6$ with increasing $H_2/C_3H_8$ feed ratio (✓Experiment)
- Maximum at higher $H_2/C_3H_8$ ratio (✓Experiment)

✓Simulation predicts positive hydrogen effect

→ Origin of 'positive hydrogen effect'?

# Variation of $H_2$ pressure



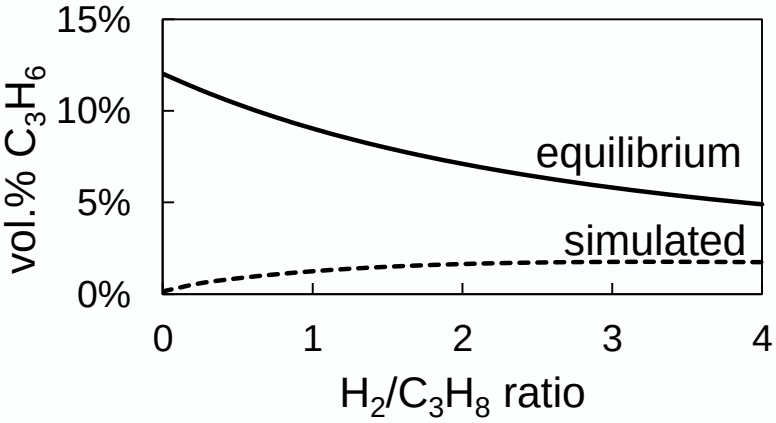

- TOF $C_3H_6$ same asymptotic behavior as free sites
- $H_2/C_3H_8$ = 0: high coverage of deeply dehydrogenated species ($CH_3C$ and CH)

$CH_3$-C and CH

$Pt_3$ $Pt_3$

ethylidyne methylidyne

- $H_2/C_3H_8$ > 0: fast decrease of these species
  → More free sites → Higher activity

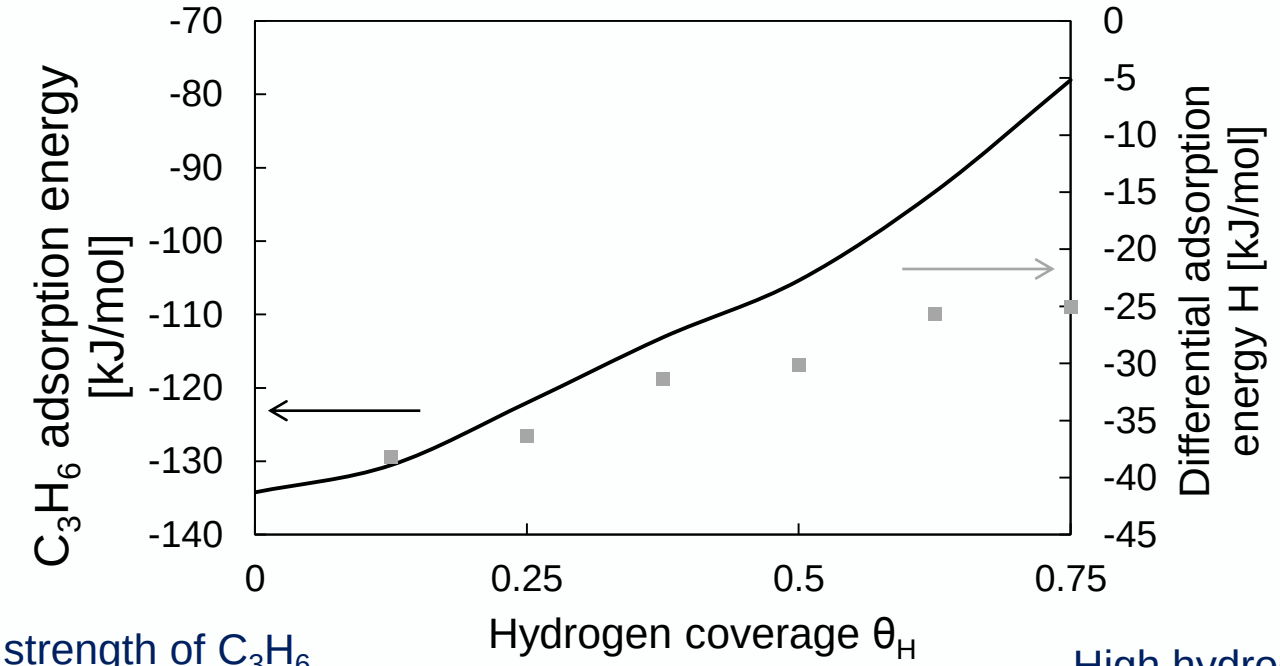



(1) Reduced blocking of active sites ✓

# Coverage dependence of energies

| | $H_2/C_3H_8$ | | | |
|---|---|---|---|---|
| | 0 | 1.25 | 3.3 | 4 |
| H | 0.4% | 18.1% | 38.0% | 42.3% |

→ Influence on adsorption strength of $C_3H_6$?




Adsorption strength of $C_3H_6$ decreases
→ Faster $C_3H_6$ desorption
→ Higher activity

High hydrogen coverage can easily be obtained

(2) Hydrogen coverage dependence of adsorption strength ✓

# Assisted H abstraction and subsurface H

## Hydrogen assisted β-hydrogen abstraction

e.g. $CH_2(Pt)\text{-}CH_2\text{-}CH_3$ + $H(Pt)$ → $CH_2(Pt)\text{-}CH(Pt)\text{-}CH_3$ + $H_{2,(g)}$ → No transition state is found

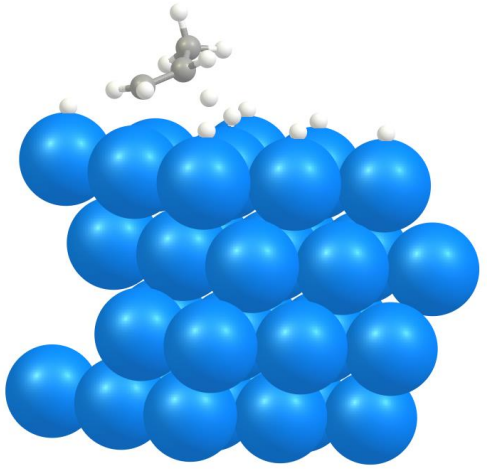
1-propyl

propylene

$CH_2(Pt)\text{-}CH_2\text{-}CH_3$ + 7 $H(Pt)$ → $CH_2(Pt)\text{-}CH(Pt)\text{-}CH_3$ + 8 $H(Pt)$ →

1-propyl

propylene



Barrier ~70 kJ/mol higher

(3) Hydrogen-assisted β-hydrogen abstraction ✗

## Subsurface hydrogen

$CH_2(Pt)\text{-}CH_2\text{-}CH_3$ + 9 $H_{subsurface}$ → $CH_2(Pt)\text{-}CH(Pt)\text{-}CH_3$ + $H(Pt)$ + 9 $H_{subsurface}$ → No influence on reaction barrier

propylene

(4) Subsurface hydrogen ✗

# Conclusions

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2$$

- Co-feeding $H_2$ has positive effect on activity → Experiment (Siddiqi et al. 2010)
- Perform DFT calculations with extended reaction network
- Possible explanations:

  (1) Less deeply dehydrogenated species → More free sites ✓

  (2) Coverage dependence of energies ✓

  (3) Hydrogen assisted β-hydrogen abstraction ✗

  (4) Subsurface hydrogen ✗

# Acknowledgments


- The Long Term Structural Methusalem Funding by the Flemish Government.
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# Glossary

- **Positive hydrogen effect**: the positive effect on activity of co-feeding hydrogen with propane in the catalytic propane dehydrogenation reaction.
- **Turnover frequency**: number of times the reaction proceeds per second per active site on the surface.
- **Coke precursors**: deeply dehydrogenated species on the surface that eventually will block the active sites of the catalyst, e.g. methylidyne ($CH{\equiv}Pt_3$).

# Back-up slides

# Back-up 1

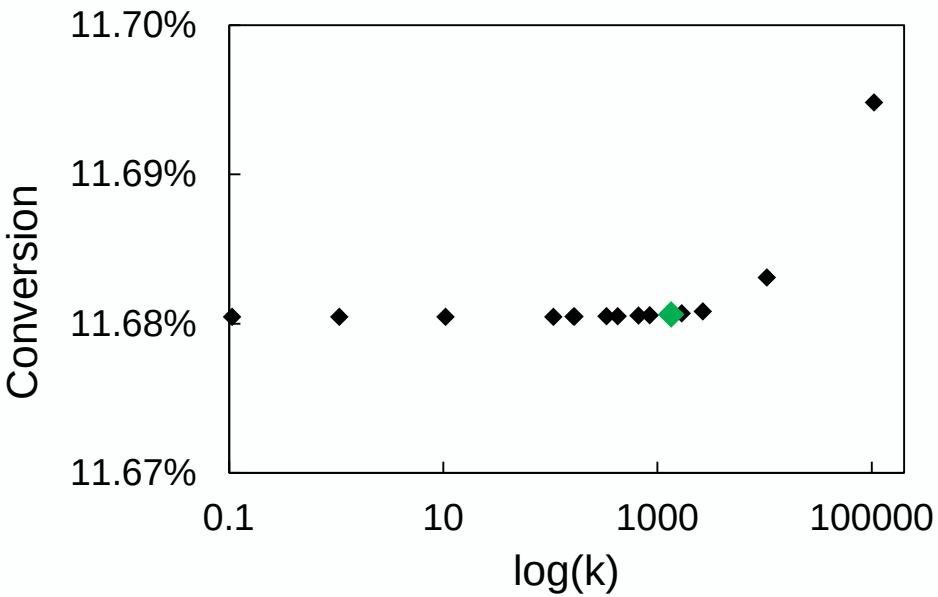
## Determine rate coefficient *k*

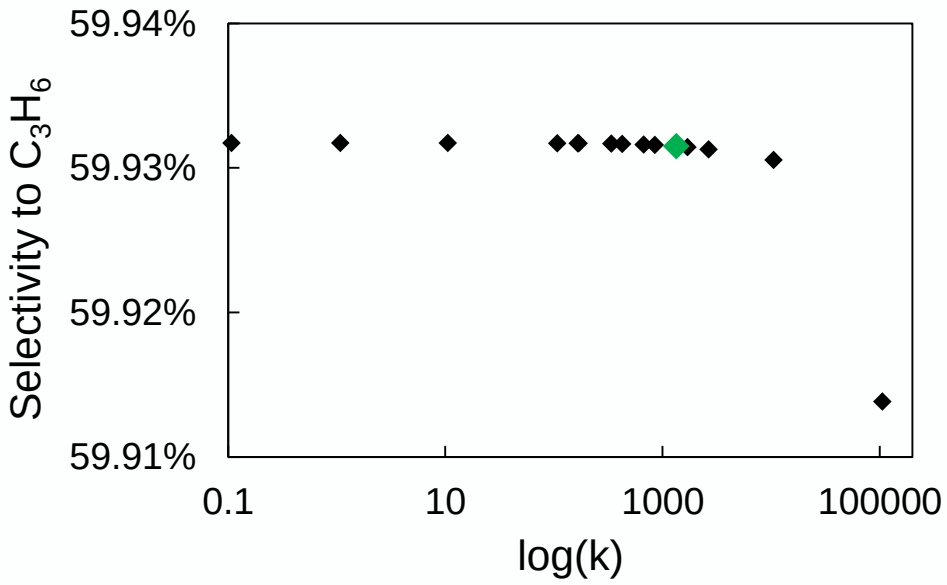
C → coke formation
III
$Pt_3$

| | Temperature (K) | Coke formation (5' TOS) ($mol_C/mol_{Pt}$) | |
|---|---|---|---|
| | | Experiment | Simulated |
| Siddiqi (2010) | 873 | 32.0 | 32.6 |

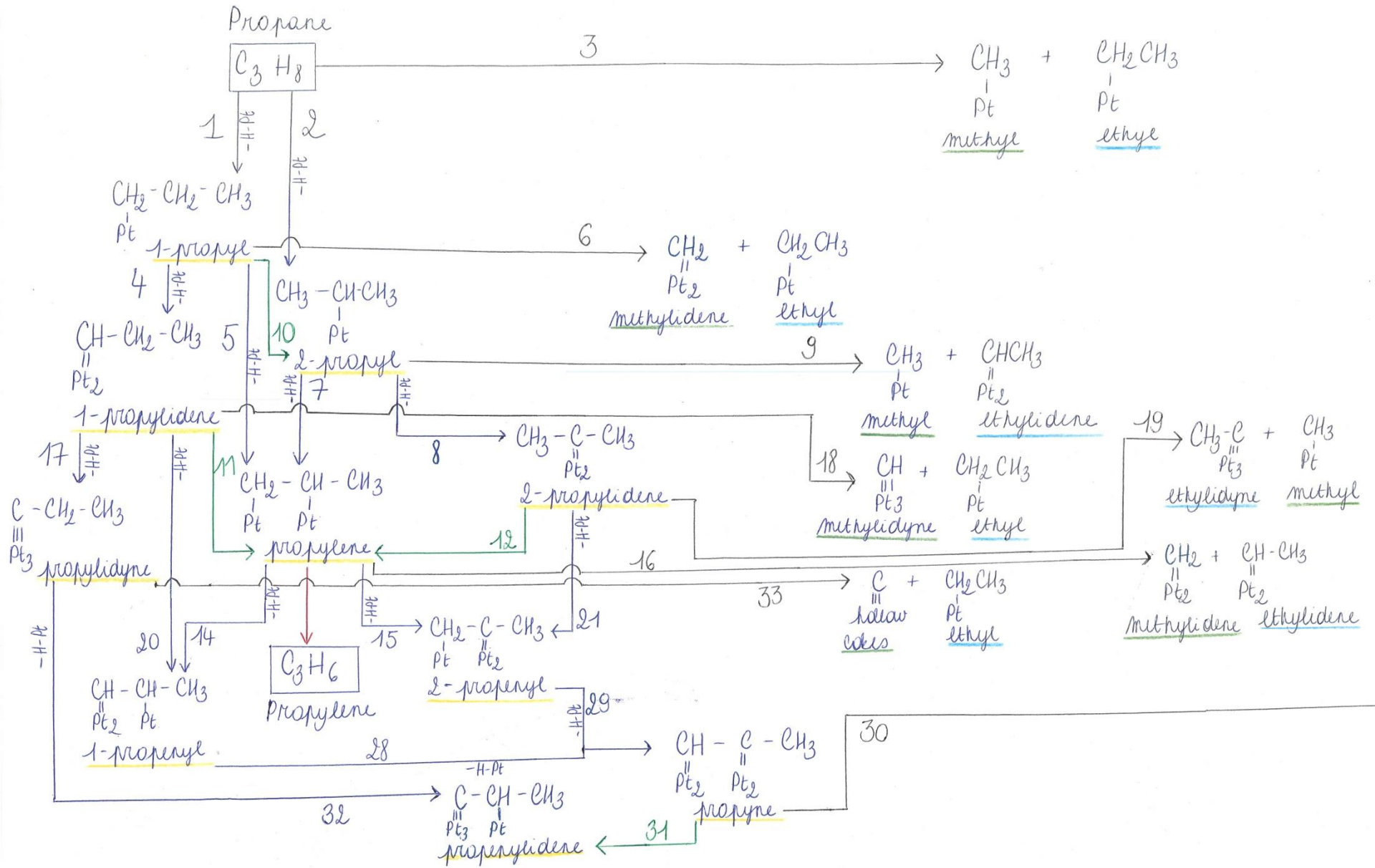
using $k = 1.25 \cdot 10^3\ s^{-1}$ gives good agreement with experiment

✓ Limited influence on conversion/selectivity

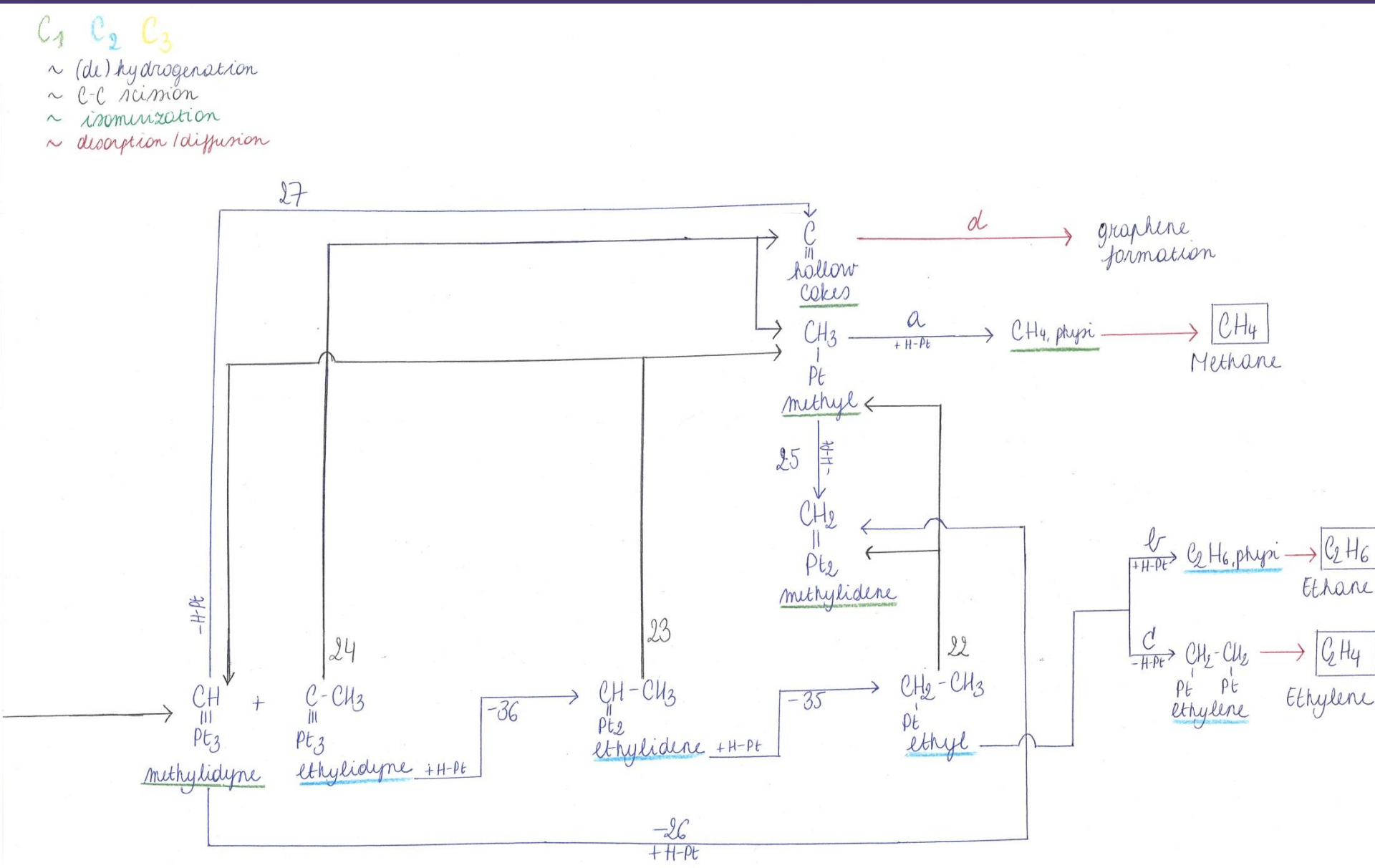


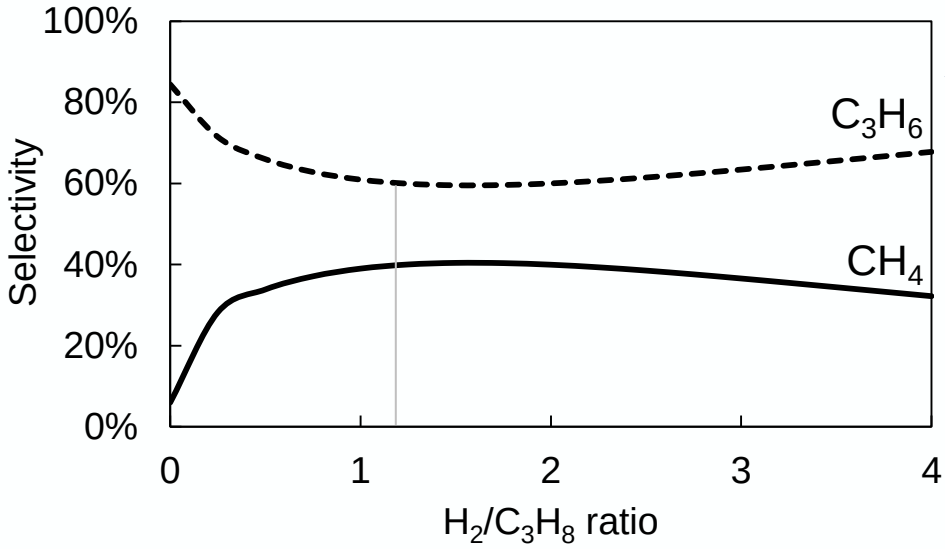
# Back-up 2


Propane
C3 H8
1
2
3
CH3 + CH2CH3
Pt
methyl
ethyl
CH2-CH2-CH3
1-propyl
6
CH2 + CH2CH3
Pt2
methylidene
4
CH-CH2-CH3
5
CH3-CH-CH3
10
2-propyl
9
CH3 + CHCH3
ethylidene
1-propylidene
7
8
CH3-C-CH3
17
11
CH2-CH-CH3
18
CH + CH2CH3
methylidyne
19
CH3-C + CH3
ethylidyne
C-CH2-CH3
propylidyne
2-propylidene
12
propylene
16
CH2 + CH-CH3
methylidene
ethylidene
33
C + CH2CH3
solid
coke
20
14
15
CH2-C-CH3
21
2-propenyl
C3H6
Propylene
CH-CH-CH3
1-propenyl
29
28
CH-C-CH3
propyne
30
32
C-CH-CH3
propenylidene
31

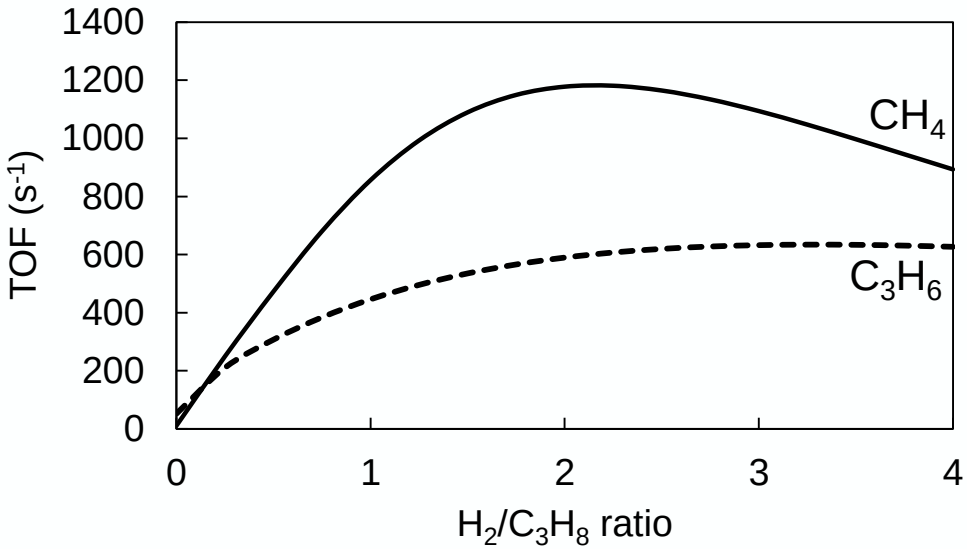
# Back-up 3


C1 C2 C3
~ (de) hydrogenation
~ C-C scission
~ isomerization
~ desorption / diffusion
27
C
hollow
coke
d
graphene
formation
CH3
Pt
methyl
a
+H-Pt
CH4, physi
CH4
Methane
25
-H-Pt
CH2
Pt2
methylidene
b
+H-Pt
C2H6, physi
C2H6
Ethane
c
-H-Pt
CH2-CH2
Pt Pt
ethylene
C2H4
Ethylene
-H-Pt
CH
Pt3
methylidyne
+
24
C-CH3
Pt3
ethylidyne
+H-Pt
-36
23
CH-CH3
Pt2
ethylidene
+H-Pt
-35
22
CH2-CH3
Pt
ethyl
-26
+H-Pt

# Back-up 4

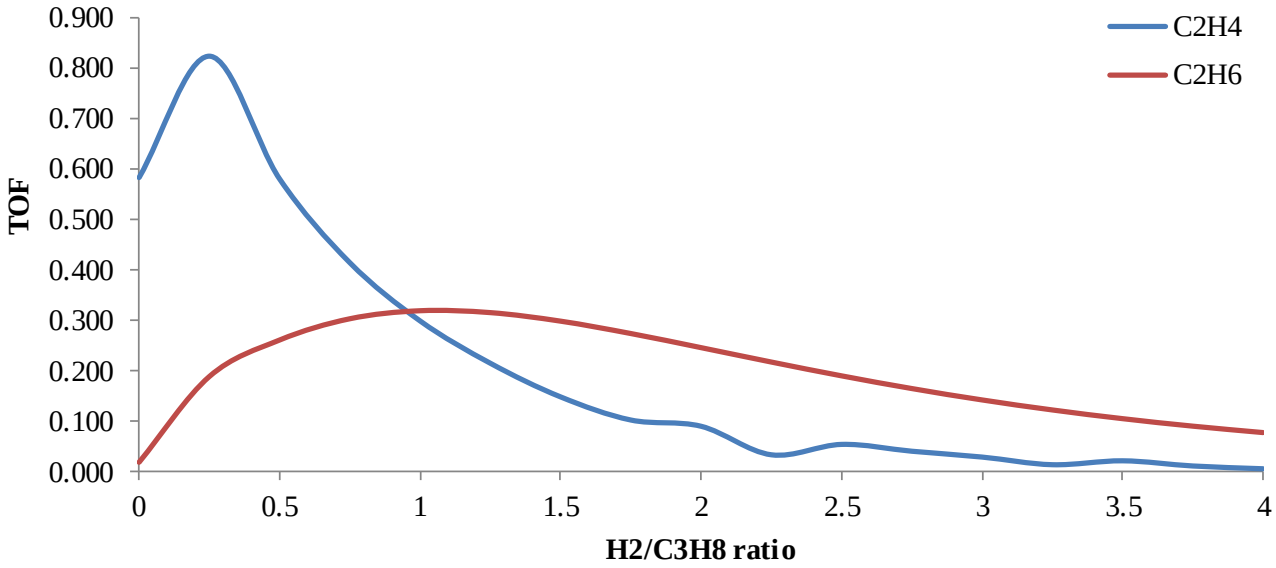


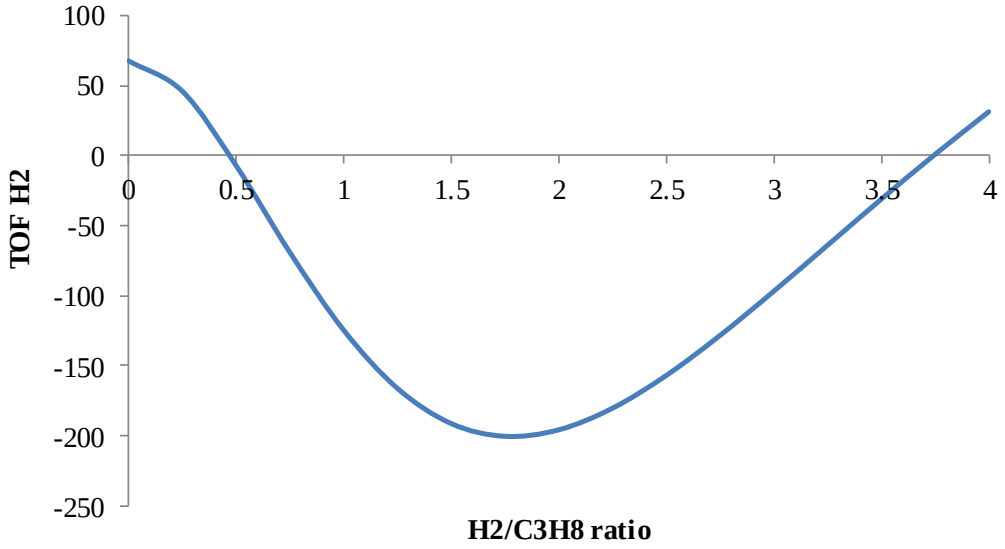

← High selectivity to $C_3H_6$ at all $H_2/C_3H_8$ feed ratios (✓Experiment)



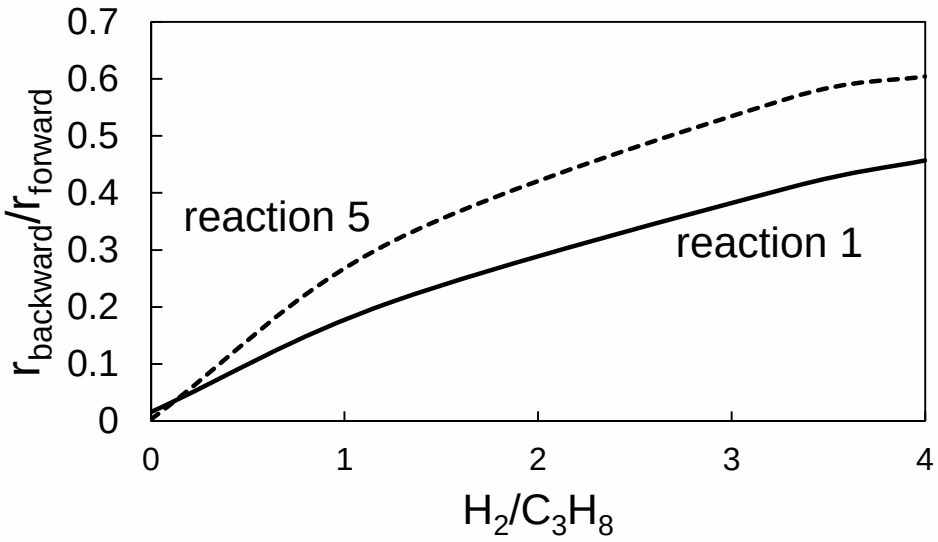

← TOF $CH_4$ and $C_3H_6$

# Back-up 5


C2H4
C2H6
TOF
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
0.5
1
1.5
2
2.5
3
3.5
4
H2/C3H8 ratio


TOF H2
100
50
0
-50
-100
-150
-200
-250
0
0.5
1
1.5
2
2.5
3
3.5
4
H2/C3H8 ratio

# Back-up 5




← Closer to equilibrium

# Back-up 6

**Table 3-1. Comparison of propylene/propane adsorption strength for two different functionals and experiment.**

| $\Delta E_{ads}$ (kJ/mol) | Experimental data (0.2 ML) [24] | OptPBE vdW-DF (0.13 ML) | BEEF vdW-DF (0.13 ML) |
|---|---|---|---|
| Propylene chemisorption | -68 | -134 | -105 |
| Propane physisorption | - | -43 | -33 |